Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

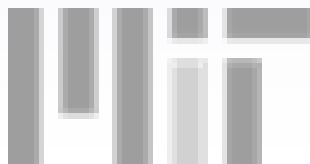### *Ocean Sequestration*

Scale-up of CO$_2$ Hydrate Particle Formation for Ocean Carbon Sequestration

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Marine Injection of CO_2: Background

- Marine sequestration of CO_2 is a possible method to counteract the increase in atmospheric CO_2.

- Costs of methods increase with injection depth. Residence times of sequestered CO_2 increase with increasing depth.

- Using hydrate formation to sequester CO_2 will decrease costs by decreasing depth necessary for injection.

Concept of CO$_2$ Hydrate for Ocean Sequestration

Pressure/Depth versus Density

Dispersed Phase

Continuous Phase
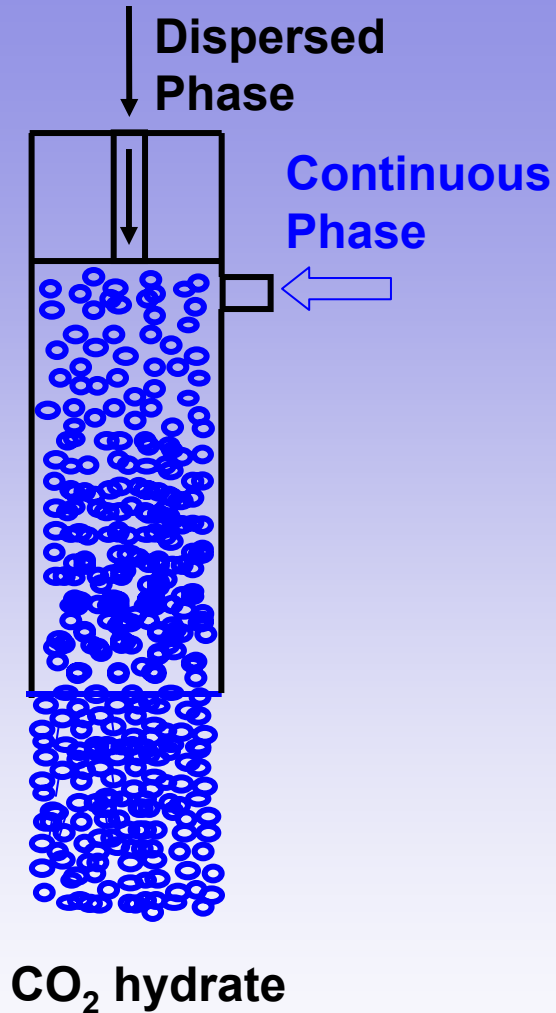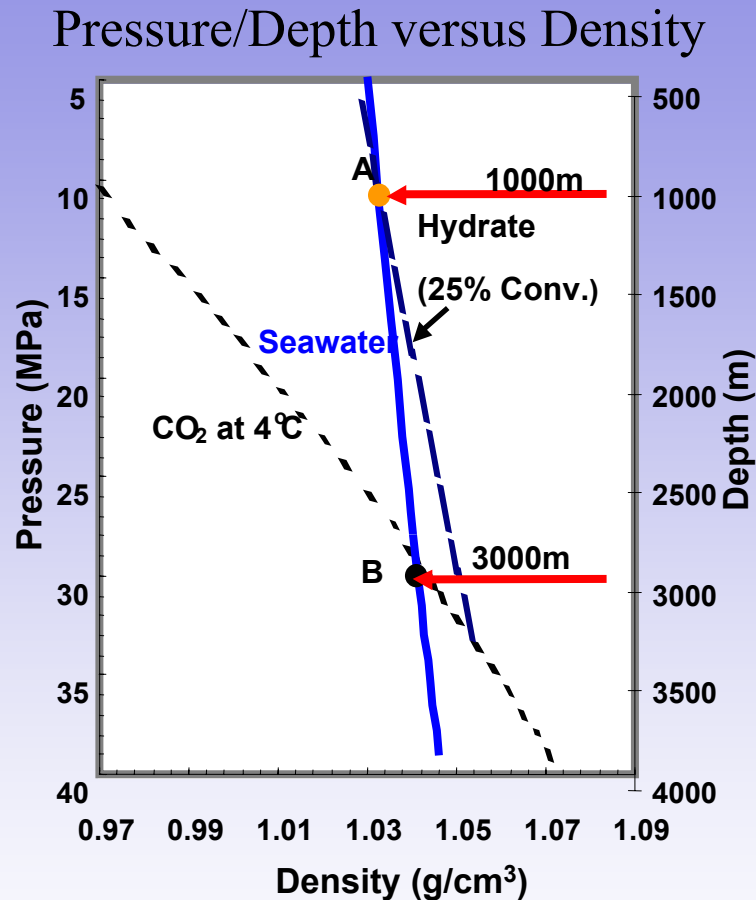
CO$_2$ hydrate

- The density of the composite produced depends highly on the conversion of liquid CO$_2$ to hydrate.

West et al., AIChE J., 2003

Objective of this Part
of CO_2 Hydrate Injection

- Previous field and laboratory studies demonstrated the concept of injecting CO_2 hydrate particles at a shallow depth for ocean sequestration.

- The objective of this research is to test a larger-scale continuous-jet hydrate reactor.

- This reactor increases CO_2 flowrate by approximately two orders of magnitude.

Methods Used in Laboratory at ORNL

**The ORNL SPS
(Seafloor Process Simulator)**

**The ORNL
Continuous-jet
Hydrate Reactor**

- 72 L Volume
- Hastelloy
- Pressures up to 20 MPa
- Temperatures 0°C and up
- 41 sampling ports

The Continuous-Jet Hydrate Reactor: Geometry and Conditions II
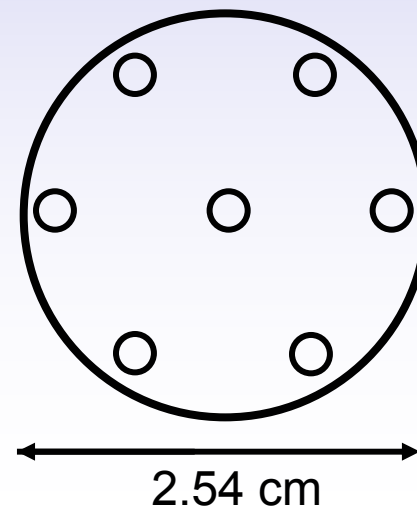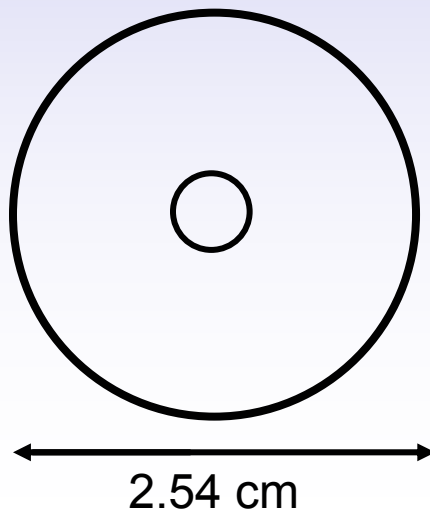
Injector side-view

2.54 cm

45.7 cm
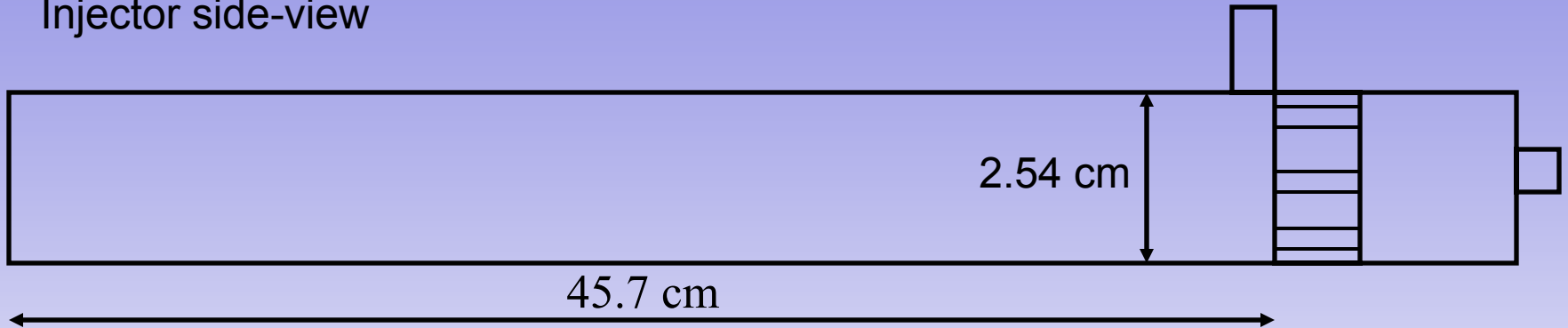
Capillary plan-view

2.54 cm

2.54 cm

The Continuous-Jet Hydrate Reactor: Geometry and Conditions I

- This reactor allows different capillary sizes to be used.
  - Single-capillary: 2.381-mm, 3.175-mm, and 3.969-mm
  - Multiple-capillary: 0.379-mm, 0.794-mm, 1.191-mm, and 1.588-mm.
- Variable flow rates for both liquids were tested.
  - Water: between ~0.80 and ~3.00 L/min water
  - CO_2: between ~0.33 and ~0.66 L/min CO_2 (pulsed)
- Pulsed CO_2 flow duration is equivalent to CO_2 ~5.5 L/min.
- Temperatures: 1.5 to 5°C
- Pressures: 4.8 to 13.1 MPa
- Experiments were conducted in both distilled and saline water.

Summary of Parameters Investigated

- Bouyancy

- Pressures and Temperature

- Dispersed v. continuous phases

- Capillary size

- Capillary configuration (multiple or single capillary)

- Water chemistry

- Dissolution rates of produced hydrate

Experimental Results

- Liquid CO_2/water/ CO_2-hydrate consolidated composite particles were successfully produced in the laboratory.

- All capillary sizes and configurations yielded hydrates with varying buoyancies and levels of consolidation.

- Consolidated composites were formed at pressures as low as 4.8 MPa.

Effects of CO_2 v. Water as Dispersed Phase I

- Buoyancy differences were observed between hydrate produced using water or CO_2 as the dispersed phase.

  - Experiments using water as the dispersed phase typically produced floating hydrate.

  - Experiments using CO_2 as the dispersed phase typically produced sinking hydrate.

  - This behavior is due to the pulsed flow of CO_2.

Liquid CO_2
Water

Liquid CO_2

Water

CO_2 hydrate
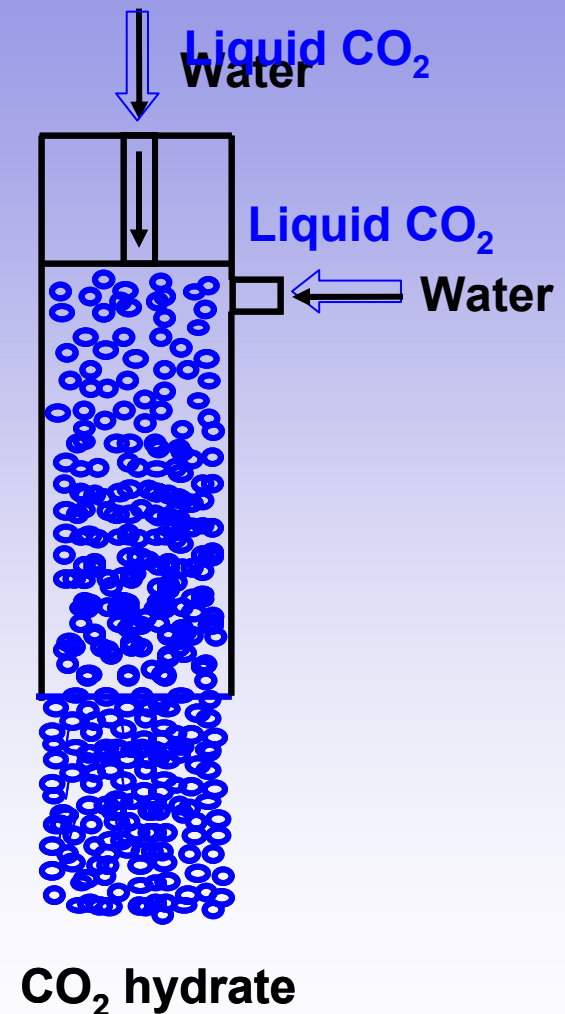
Effects of CO_2 v. Water as Dispersed Phase II

- Clogging problems were not observed during testing of the injector, as apposed to previous experiments with smaller injectors.

- Using water as dispersed phase produced sinking composite only at pressures exceeding 13.1 MPa (~1300 m).

- Using CO_2 as dispersed phase produced composites with greater density.

Effect of Capillary Size I

- Smaller capillary sizes typically produced more consolidated and dense hydrate composite.

- Reynolds Number: $Re = 4\rho Q/\pi d^o \mu$
  - The ratio of inertial forces to viscous forces.

  Ohnesorge Number: $Z = \mu/(\rho\sigma d^o)^{0.5}$
  - The ratio of viscous forces to surfaces forces.

- This can be attributed to greater Reynolds and Ohnesorge numbers associated with smaller capillary sizes.

Effect of Capillary Size II

Dispersed Phase	Capillary Diameter (mm)	Pmin (MPa)	Temp (°C)
	Single Capillary		
Distilled Water	3.175	sinking not observered	4.5
	3.969	sinking not observered	4.5
	Multiple Capillary		
	1.191	13.1	2.5
	1.588	sinking not observered	4.0
	Single Capillary		
	2.381	7.6	5.0
	3.175	sinking not observered	4.0
	Multiple Capillary		
Liquid CO_2	0.397	6.2	4.2
	0.794	6.2	3.5
	1.191	6.9	5.1
	1.588	7.6	3.3

Effect of Capillary Configuration: Multiple or Single-Capillary

- Results from multiple and single-capillary configurations with similar total cross-sectional areas were compared.

- These results indicated that multiple-capillaries produce more dense and consolidated composite. This is probably due to smaller droplet size.

Comparison of Single and Multiple-capillaries with Similar Total Cross-Sectional Area
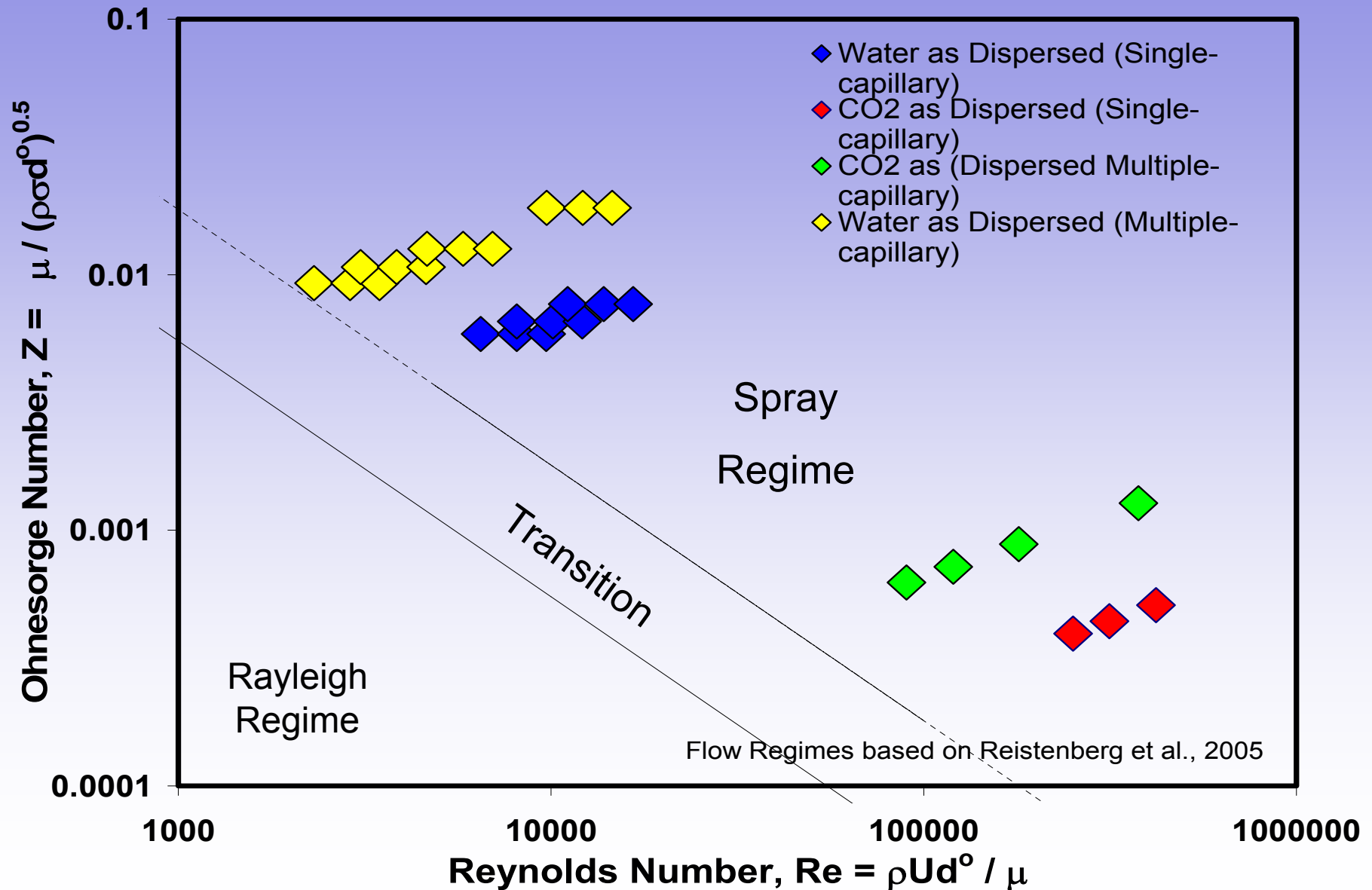
| Pmin | Water Flow | CO_2 Flow | Single Capillary | | | Multiple Capillary | | |
| | | | Temp | Diameter | | Temp | Diameter | |
MPa	L/min	mL/min	°C	mm	Behavior	°C	Mm	Behavior
11.7	2.00	0.33	4.0	3.175	C NB	4.4	1.191	C S
11.7	2.00	0.40	4.0	3.175	C F	4.4	1.191	C S
11.7	2.00	0.50	4.0	3.175	U F	4.4	1.191	C S
11.7	2.00	0.66	4.0	3.175	U F	4.4	1.191	C S
11.7	2.50	0.33	4.0	3.175	C NB	4.4	1.191	U S
11.7	2.50	0.40	4.2	3.175	C NB	4.4	1.191	C S
11.7	2.50	0.50	4.2	3.175	U NB	4.4	1.191	C S
11.7	2.50	0.66	4.2	3.175	U F	4.4	1.191	C S
11.7	3.00	0.33	4.2	3.175	NB C	4.4	1.191	C S
11.7	3.00	0.66	4.2	3.175	C F	4.4	1.191	C S
10.3	3.00	0.66	3.9	3.175	U F	5.1	1.191	C S

U = Unconsolidated, C = Consolidated, S = Sinking, NB = Neutrally Buoyant, F = Floating
1.191-mm multiple-capillary = 7.795 mm^2 and 3.175 single-capillary = 7.913 mm^2

- Hydrate produced using a multiple-capillary has a greater density than composite produced using a single-capillary of similar total cross-sectional area.

Reynolds and Ohnesorge Numbers for Different Dispersed Phases.

Ohnesorge Number, $Z = \mu / (\rho \sigma d^o)^{0.5}$

Reynolds Number, $Re = \rho U d^o / \mu$

- ◆ Water as Dispersed (Single-capillary)
- ◆ CO_2 as Dispersed (Single-capillary)
- ◆ CO_2 as (Dispersed Multiple-capillary)
- ◆ Water as Dispersed (Multiple-capillary)

Spray Regime

Transition

Rayleigh Regime

Flow Regimes based on Reistenberg et al., 2005

Effect of Water Salinity I

- The scale-up reactor was tested using saline and distilled water.

- The reactor produced negatively buoyant and consolidated hydrate in both saline and distilled water.

- Saline water increases the pressure and decreases temperature necessary to produce sinking hydrates.

Effect of Water Salinity II

| Saline Water				Distilled Water			
Pmin	Temp	Water Flow	Behavior	Pmin	Temp	Water Flow	Behavior
MPa	°C	L/min		MPa	°C	L/min	
13.1	1.9	2	C S	4.8	4.2	2	U F
13.1	1.9	3	C S	6.2	4.2	2	U NB
11.7	1.5	2	C S-NB	6.7	4.1	2	C S
11.7	1.6	3	C S	7.6	4.1	2	C S
11.7	3	2	C NB	9	5.2	2	C S
11.7	2	2	C S-NB	10.3	5.1	2	C S
11.7	3.5	2	C F	11.7	4.4	2	C S
13.1	4.7	2	C F	13.1	3.5	2	C S

C = consolidated, F = floating, NB = neutrally buoyant, S = sinking, and U = unconsolidated. Pmin = minimum pressure required to produce sinking composites. CO_2 flowrates all at 0.66 L/min

- Increasing water salinity lowered temperature and increased pressure necessary for producing sinking composite.

CO$_2$ Hydrate Dissolves as it Descends in Seawater
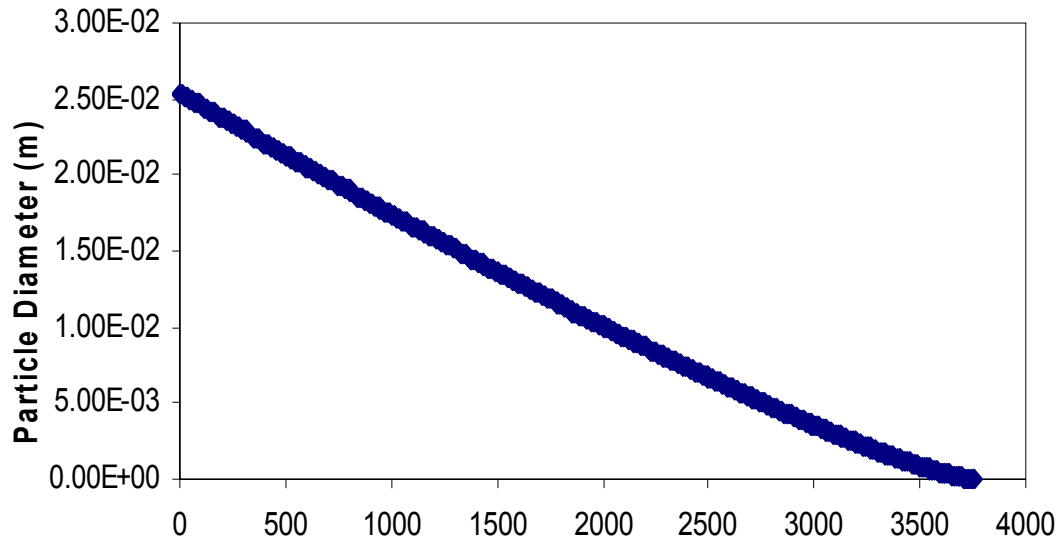
Mass-transfer modeling based on single particle
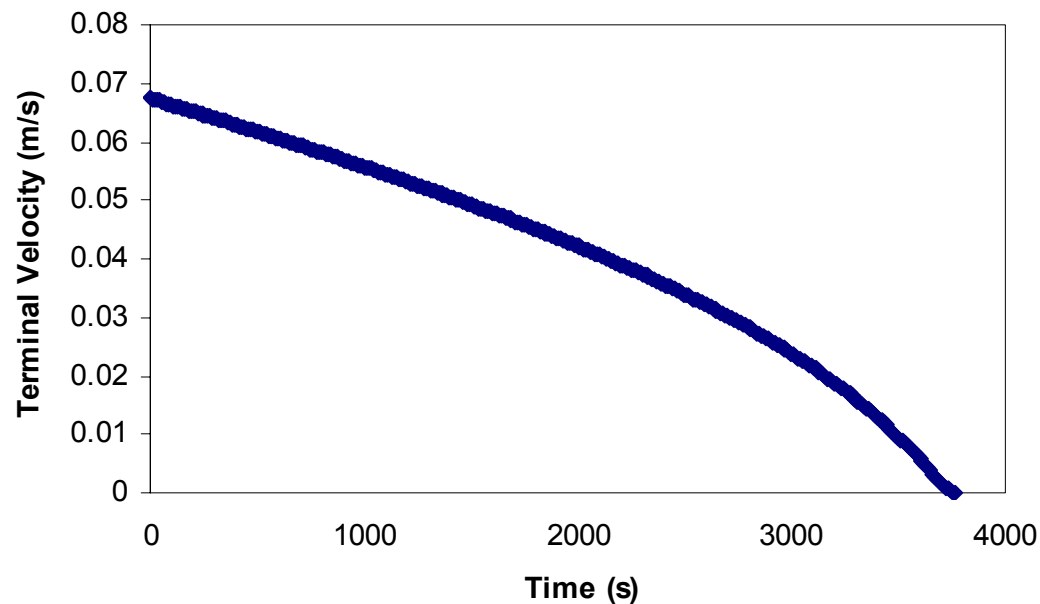
Additional effects occur in a plume allowing the particles to descend for as much as 1000 m before dissolution:
• Solute density effect: Seawater density increases due to CO$_2$ dissolution
• Plume effect: Particles sink with plume velocity plus settling velocity
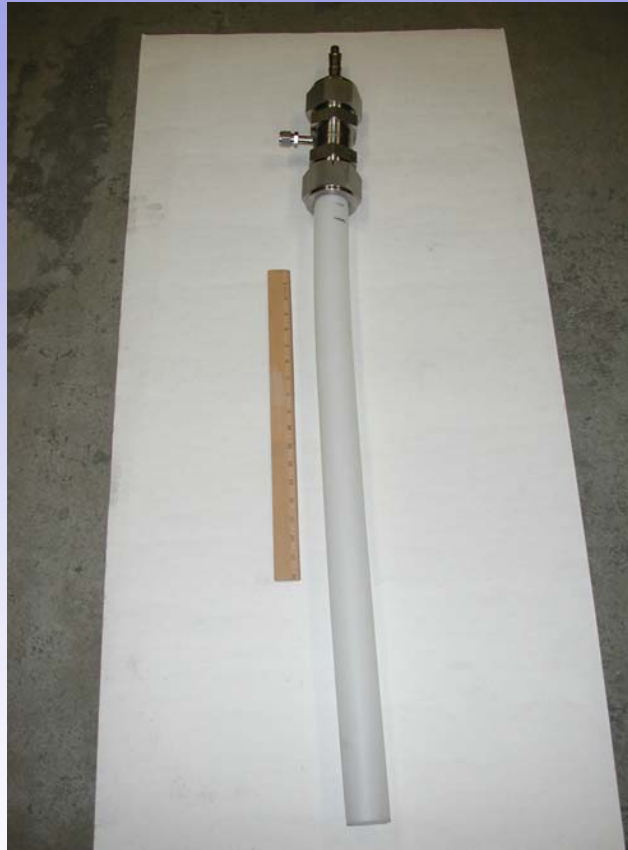
Riestenberg et al., ES&T, 2005

Summary

- A scaled up continuous-jet hydrate reactor was successfully developed and used to form hydrate composite particles.

- Optimum operation conditions at intermediate ocean depths for the continuous-jet hydrate reactor were determined.

- Ideal conditions for producing negatively buoyant composites include the use of a multiple-capillaries, pulsed CO_2 flow, temperatures of 2.0-3.0°C, and pressures ~ 11.7 MPa.

Acknowledgment

Ongoing Research

Ongoing Research